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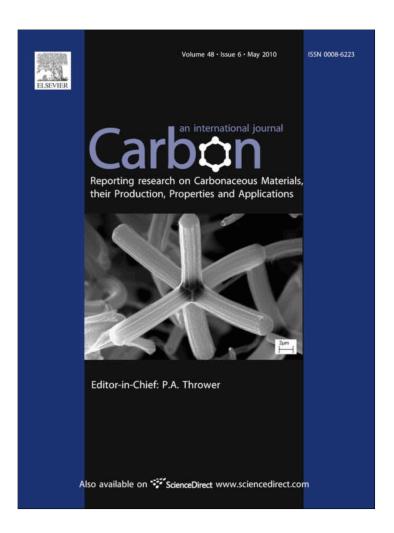
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# The effect of oxidation on the surface chemistry of sulfurcontaining carbons and their arsine adsorption capacity

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#### ABSTRACT

Two carbons with different sulfur contents were prepared and oxidized either by heating in air or by chemical treatment. The samples were then tested as adsorbents of arsine in dynamic conditions at room temperature, both in dry conditions and in the presence of moisture. Chemical and structural features of the initial and arsine-exposed materials were analyzed by energy dispersive X-ray spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analyses, sorption of nitrogen and sorption of water. It was found that oxygen- and sulfur-containing groups participate in arsine oxidation to arsenic tri- and pentoxide and/or in the formation of arsenic sulfides. This occurred either via activation of oxygen or a direct involvement of these groups in reactions with arsine. A very hydrophilic surface of sulfur-containing carbons, which causes the presence of adsorbed water, even in dry conditions, enhances arsine removal. On the other hand, in moist conditions water totally occupies the pore system blocking the catalytic action of the surface toward oxidation, which leads to a very limited or zero AsH<sub>3</sub> adsorption capacity.

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#### 1. Introduction

Removal of arsine from a gas phase is an important issue for the semiconductor industry and also for catalytic processes, which utilize syngas. Arsine in the synthetic gas is considered as a catalyst poison for such processes as, for example the liquid phase methanol production. To preserve catalyst efficiency, even the traces of AsH<sub>3</sub> should be removed. Besides the technological difficulties, arsine is also a powerful toxin susceptible to oxidation with a strong exothermic effect. Of all the methods to separate arsine from either air or syngas adsorption is the most common.

The addition of copper species is described as effective in promoting arsine adsorption [1] on either alumina or activated carbons supports [1–3]. It was found that copper oxide, CuO, distributed on a support surface leads to the deposition of arsine as Cu<sub>3</sub>As or elemental arsenic. In addition to CuO,

oxides of silver, manganese, nickel and zinc have been used on alumina supports [3]. On activated carbons such oxides as CuO and  $CrO_3$  were deposited to promote arsine oxidation. This process led to the reduction of copper (Cu(II)) to metallic copper and Cr(VI) to Cr(III) [4]. Another impregnant shown to remove arsine on carbon was copper (II) chromite, which is converted to  $Cu_3As_2$  and  $Cr_2O_3$  in surface reactions [5]. It must be recalled that molecular oxygen is not present in syngas.

A comparative study of arsine removal from syngas on various adsorbents was carried out by Quinn and co-workers [1]. Commercial adsorbents with alumina or carbon supports were investigated with oxides of lead, manganese, copper, silver, chromium and their mixtures, and metallic copper deposited on their surfaces. On a carbon adsorbent with CuO, the adsorption was enhanced at high temperature (140 °C). It was indicated that at ambient conditions the diffusion of arsenic from the copper surface and into the bulk met-

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als limited the removal process. When  $AsH_3$  removal was tested on carbon with metallic copper, besides  $Cu_3As$ , hydrogen was also produced. Quinn and co-workers suggested that oxygen groups on the carbon surface provide active sites for  $AsH_3$  binding [1]. The precise role of those centers was not explored.

Application of activated carbons as supports for cupric oxide in the removal of arsine from air had been addressed in the 1940s in research related to chemical warfare protection. Hickey and Wiig found that on such carbons, arsenic trioxide was the main product of surface oxidation and that cupric oxide worked as an oxidation catalyst [6]. Water, which is always present in the moist air, was found as either an inhibitor or promoter of adsorption. The authors indicated that when water is in the air stream in addition to arsine (and thus not already adsorbed on the carbon surface), it can adsorb at the active sites faster than arsine. The chemical/ physical nature of those centers was not revealed. On the other hand, at low humidity level, adsorption was promoted resulting in over 100% increase. The capacity on virgin carbons was found to be negligible in comparison with cupric acid containing carbons on which about 130 mg of AsH<sub>3</sub> per cm<sup>3</sup> of adsorbent (or about 270 mg/g) was retained at dry conditions.

The objective of this paper is to investigate the role of oxygen and sulfur-containing groups on non-impregnated activated carbons in the retention/oxidation of arsine. Recently, the carbon surfaces, containing heteroatoms such as oxygen, nitrogen and sulfur, were found to be active in oxidation [7–9]. This is caused by an activation of oxygen to superoxide, which is catalyzed by surface functional groups [10,11]. Taking this into account, our target is to investigate the role of carbon surface heterogeneity (chemical and physical) in the reactive adsorption of arsine in dry and wet conditions. Polymer-derived carbons with incorporated sulfur, and free of any additional inorganic matter, were further oxidized to broaden the spectrum of surface chemistry and porosity. The products of surface reactions occurring as a result of arsine exposure to these samples were studied with emphasis on the role of a carbon surface.

#### 2. Experimental

#### 2.1. Materials

Two series of polymer-based carbons were prepared. The polymer precursors for these two series were poly(4-styrene sulfonic acid co-maleic acid), sodium salt and poly(sodium 4-styrene sulfonate). Carbon samples were obtained according to the method described in Ref. [12] and the features of these materials are presented in detail in Ref. [9]. Briefly, both polymers were carbonized at 800 °C for 40 min under nitrogen, in a horizontal furnace. Obtained carbons were oxidized either in a solution of ammonium persulfate (method A) or in air at 350 °C (method B). After washing and drying, the samples are referred to as C-1A, C-1B, C-2A and C-2B, where C-1 denotes the carbons obtained from poly(4-styrene sulfonic acid co-maleic acid), and C-2 obtained from poly(sodium 4-styrene sulfonate). "A" represents oxidation in ammonium persulfate and "B"— in air.

#### 2.2. Methods

#### 2.2.1. AsH<sub>3</sub> breakthrough dynamic test

A micro-scale breakthrough apparatus was used to determine arsine adsorption at equilibrium. In a typical test, a small amount of adsorbent (50-80 mg) was packed into a fritted glass tube (Dynatherm Sampling Tube, CDS Analytical Inc.). The temperature of the bed was controlled using a thermostatted bath. The inlet stream was delivered from a pressured gas mixture prepared from 4% arsine in nitrogen (Matheson Gas Products Inc.) and the total flow rate was equal to 20 mL/min. The breakthrough of arsine was monitored by a FT-IR spectrometer. Experiments were conducted both in dry conditions and in the presence of water. The controlled humidity was established by mixing water saturated and dry air streams. The conditions of the experiment were selected to minimize dead time response, while not offering excessive pressure drop. The suffixes -ED and -EM are used to refer to the exhausted samples on which arsine was adsorbed in dry and moist conditions, respectively.

#### 2.2.2. Adsorption of water

Water adsorption isotherms were determined using an automated gravimetric apparatus. Prior to the test, samples were heated and purged in nitrogen. The apparatus was comprised of three computer-controlled subsystems: the vapor-phase concentration control, the adsorbed-phase measurement, and the temperature-control systems. A double pass contactor, using an aluminum oxide thimble, was used to generate a saturated water stream at a fixed temperature. Dry air was mixed with the saturated air to generate a known humidity and then was directed to a microbalance (Cahn D-200, Thermo Inc.) with 1.0  $\mu g$  sensitivity and 100 mg range. The weighing basket was enclosed in a thermostatted chamber. The basket temperature was measured using a thermocouple. All other streams were air.

#### 2.2.3. EDX

Energy dispersive X-ray (EDX) data were obtained with a Zeiss Supra 55 instrument. The instrument has a resolution of 5 nm at 30 kV. Scanning was performed on the dried samples. From EDX analyses, the content of elements on the surface was calculated and the maps of the elements derived.

#### 2.2.4. XRD

X-ray diffraction (XRD) measurements were conducted using standard powder diffraction procedures. Adsorbents were ground with methanol in a small agate mortar. The mixture was smear-mounted and then analyzed by Cu  $K\alpha$  radiation generated in a Phillips X'Pert X-ray diffractometer. A standard glass slide was run for the background.

#### 2.2.5. FT-IR

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet Magna-IR 830 spectrometer using the attenuated total reflectance method (ATR). The spectrum was generated and collected 16 times and corrected for the background noise. The experiments were done on the powdered samples, without KBr addition.

#### 2.2.6. Thermal analysis

Thermogravimetric (TG) curves were obtained using a TA instrument thermal analyzer. The initial samples were exposed to an increase in temperature of 10 °C/min while the nitrogen flow rate was held constant at 100 mL/min. From the TG curves, differential TG (DTG) curves were derived.

#### 2.2.7. pH

The surface pH of the initial and exhausted samples was measured. About 0.025 g of the carbon powder was stirred for 10 h with 10 mL deionized water and then the pH of the suspension was recorded.

#### 2.2.8. Sorption of nitrogen

Nitrogen isotherms were measured at  $-196\,^{\circ}\text{C}$  using an ASAP 2010 instrument (Micromeritics). Prior to each measurement, initial and exhausted samples were outgassed at 120  $^{\circ}\text{C}$  to vacuum 10 Torr. Approximately 0.10 g of sample was used for these analyses (0.05 g for the exhausted samples). The surface area,  $S_{\text{BET}}$  (Brunauer–Emmet–Teller, BET method), the micropore volume,  $V_{\text{mic}}$ , (Dubinin–Radushkevitch method, D–R [13]), the mesopore volume,  $V_{\text{mes}}$ , and the total pore volume,  $V_{\text{t}}$ , were calculated from the isotherms. Density Functional Theory (DFT) was used to calculate the pore size distributions [14].

#### 3. Results and discussion

Arsine removal capacities on our samples are presented in Table 1. As seen, capacities measured in dry conditions are very high and in the case of C-1B and C-2B, they are much higher than those reported by Hickey and Wiig on cupric oxide containing carbons [6]. Oxidation in air results in a much higher capacity than that measured on the carbon oxidized with ammonium persulfate. In moist conditions, the capacity is almost nil and only small quantities of arsine are retained on C-2A-EM. As a remark, breakthrough tests run in dry conditions for C-1 and C-2 carbons (results not presented here) showed the adsorption capacities of 2.7 mmol/g (211 mg/g) and 1.0 mmol/g (78 mg/g), respectively. Comparison of these results with the ones obtained for the oxidized carbons indicate the positive influence of the oxidation treatment on the arsine adsorption.

To understand the differences in the arsine removal performance, the effects of the surface features must be analyzed. Even though the surface of the carbons used in this study was described in detail elsewhere [9] to help explain ammonia adsorption, in this paper we reintroduce some data in order to link these surface features to the reactive adsorption of arsine.

Strong retention of arsine is seen on EDX element maps presented in Fig. 1 and in Table 2, where the contents of elements on the surface are listed (in weight percent "wt%", and atomic percent "at%"). From the latter, the differences in surface chemistry between unexposed carbons are seen especially in the sulfur content, which was not detected using EDX in C-1 carbons. Other studies such as XPS showed that these carbons have a small amount of sulfur, less than 1% [9]. On the other hand, the amount of sulfur in C-2A is very high and the oxidation in a liquid phase leads to twice the sulfur on the surface as in air. The percentage of oxygen in C-1 carbons is higher than that in C-2 carbons. The exposure to arsine results in the deposition of a significant quantity of arsenic on the surface and an increase in the percentage of oxygen for the C-2 carbon series. A decrease in the content of sulfur is apparent owing to an increase in the content of arsine and oxygen. An increase in the latter element could be the result of the presence of arsenic oxides or an oxidation of the carbon surface. In fact, based on a strong exothermic effect during oxidation of arsine (43.5 kcal/mol [6]), incorporation of oxygen to the carbon matrix can be a simultaneous result of arsine adsorption and oxidation. This can be also associated with the removal of some sulfur groups as was found to happen during air oxidation [9]. The decrease in sulfur for C-2B is less than that for C-2A owing to the fact that the sulfur compounds which are the most susceptible for removal (sulfonic groups) have been already removed from the surface during air oxidation [9]. The trend in the content of arsine on the surface is in agreement with the trend in the capacities measured. The analysis of the elements' maps suggests that on the surface of C-2B, besides arsenic oxides, arsenic sulfides are also present.

The X-ray diffraction patterns for the samples studied before and after arsine adsorption are presented in Fig. 2. The only visible effect of adsorption is for C-2A-ED where two well-defined diffraction peaks are revealed associated with the presence of arsenic trioxide [15]. The sizes of crystallites estimated using the Scherrer equation [16] are in order of 80 nm. It is interesting that in spite of the high adsorption on other materials studied, the crystalline form of the oxida-

Sample	AsH <sub>3</sub> remova	l capacity		рН
	(mmol/g)	(mg/g)	Initial	Exhausted
C-1A-ED	0.9	66	3.23	2.45
C-1A-EM	0	0	3.23	2.87
C-1B-ED	6.9	539	3.62	2.36
C-1B-EM	0	0	3.62	2.75
C-2A-ED	4.2	331	3.51	2.45
C-2A-EM	0.2	16	3.51	3.48
C-2B-ED	5.7	444	3.17	2.41
C-2B-EM	0	0	3.17	2.48

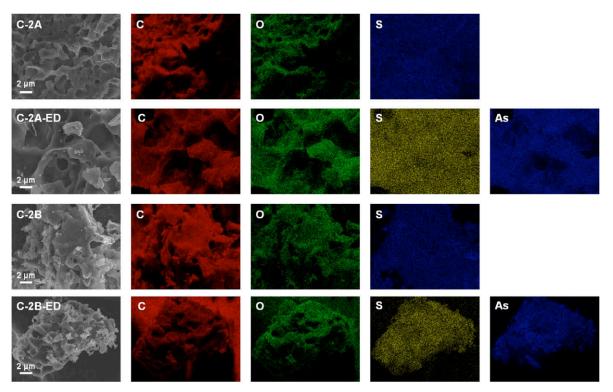


Fig. 1 - EDX maps for the C-2 series of samples before and after arsine adsorption (magnification: 6000).

Table 2 – Surfa adsorption.	ace content of	elements from	ı EDX analysis	for the C-1 ar	nd C-2 series o	f samples bef	ore and after a	arsine	
Sample		С	(	0		S		As	
	(wt%)	(at%)	(wt%)	(at%)	(wt%)	(at%)	(wt%)	(at%)	
C-1A	81.3	85.3	18.7	14.7	_	_	_	_	
C-1A-ED	71.0	83.2	16.5	14.5	-	-	12.5	2.3	
C-1B	82.8	86.5	17.2	13.5	-	_	_	-	
C-1B-ED	61.4	79.6	16.3	15.8	-	_	22.3	4.6	
C-2A	78.6	86.1	12.5	10.3	8.9	3.7	_	_	
C-2A-ED	62.9	79.1	16.6	15.6	4.0	1.9	16.5	3.4	
C-2B	83.2	88.4	12.2	9.7	4.6	1.8	_	_	
C-2B-ED	62.8	80.1	14.8	14.2	3.4	1.7	19.0	4.0	

tion products is not formed on their surfaces, or the crystals are too small to be detected.

Those oxidation products are seen on FT-IR spectra where for all exhausted samples run in dry conditions, the bands at  $800 \text{ and } 935 \text{ cm}^{-1}$  are visible (Fig. 3). They are attributed to the presence of As(V) and As(III) from arsine pent- and trioxide, respectively [17].

The oxidation products also apparently block the porosity of the materials. Table 3 presents the parameters of the porous structure for all samples. It has to be noted here that the nitrogen adsorption is measured after a pretreatment step in which samples are heated in vacuum at 120 °C, which results in the removal of any adsorbed water and weakly retained arsine. Consequently, these results reflect only the effect of the arsine adsorption and not the one of water. After adsorption, the surface area significantly decreases with increasing amount of arsine adsorbed. That decrease is very

pronounced for C-2A and C-2B, for which only about 15% of micropores and 10% of surface area are accessible for the nitrogen adsorption after the removal of arsine. For C-1 carbons, 30% of the surface is still accessible. It has to be noticed that the surface of the C-1 samples is two to three times higher than that for the C-2 series. Nevertheless, the differences in the amount of arsine adsorbed do not correspond to those differences. This is another proof that not physical but reactive adsorption governs the removal process. A decrease in the pore volume (in terms of cm³/g) for the samples oxidized in air are about 30–40% larger than for those oxidized with ammonium persulfate, which is in agreement with the higher capacities measured on the former samples.

The differences in a sample's porosity are seen in the pore size distributions presented in Fig. 4. There can be seen a bimodal distribution for the C-2 samples and quite a heterogeneous texture for the C-1 samples. Adsorption of arsine in dry

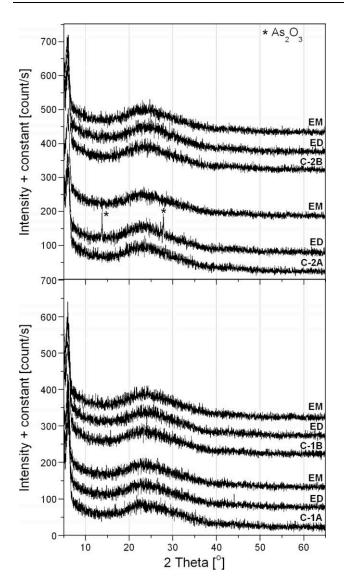


Fig. 2 – X-ray diffraction patterns for the C-1 and C-2 series of samples before and after arsine adsorption.

air affects the whole surface of the C-1 samples whereas for the C-2 series mainly micropores are affected. It is well known that the deposition of oxidation products on the microporous adsorbents may not only occur via a pore filling mechanism. The compounds retained may also block the pore entrances leaving an unused space inside. This likely happens in the case of samples run in the moist conditions for which a decrease in the volume of very small pores is noticed even though almost no capacity was measured.

Interesting results are revealed when the surface of the carbons is investigated using thermal analysis (Fig. 5). The peaks on DTG curves represent weight loss at specific temperature ranges. Apparently, in comparison with the initial samples, an increased weight loss between 150 and 600 °C is noticed after exposure to arsine. The least complex pattern on DTG curves is found for the C-1 carbons. In the case of C-1B-ED sample, an intense and relatively narrow peak is revealed with maximum at 370 °C after exposure to arsine. This peak is assigned to the sublimation of arsenic trioxide,  $\mbox{As}_2\mbox{O}_3$ 

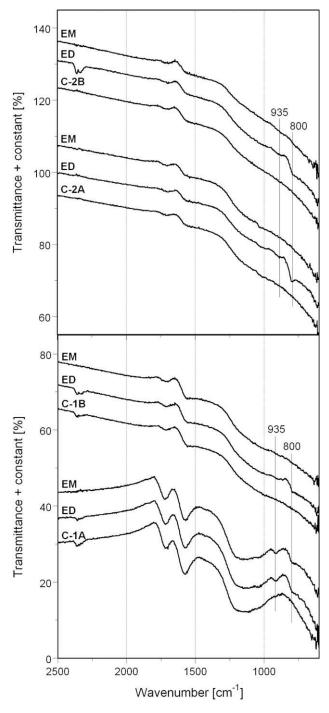


Fig. 3 – FTIR for the C-1 and C-2 series of samples before and after arsine adsorption.

(sublimates at 312 °C [18]) or arsenic pentoxide,  $As_2O_5$  (decomposition at 315 °C [18]). Nevertheless, since the peak representing sublimation of arsine at about 600 °C is not present, we hypothesize that arsenic pentoxide is not present (it would decompose to arsine) and that arsenic trioxide directly sublimates from the surface of this carbon. An additional peak at about 200 °C, revealed on the DTG curve for the sample run in the moist conditions (C-1B-EM), is linked to decomposition of  $H_3AsO_4$  leading to  $As_2O_3$  [18].  $H_4As_2O_7$  is not likely to be formed on this sample since no arsenic, from decompo-

Table 3 – The parameters of porous structure for the C-1 and C-2 series of samples before and after arsine adsorption.							
Sample	$S_{BET}$ (m <sup>2</sup> /g)	V <sub>t</sub> (cm <sup>3</sup> /g)	V <sub>meso</sub> (cm <sup>3</sup> /g)	$V_{\rm mic}$ (cm <sup>3</sup> /g)	$V_{\rm mic}/V_{\rm t}$		
C-1A	1049	0.871	0.375	0.496	0.57		
C-1A-ED	634	0.538	0.229	0.309	0.57		
C-1A-EM	1045	0.808	0.317	0.491	0.61		
C-1B	1449	1.076	0.385	0.691	0.64		
C-1B-ED	595	0.478	0.216	0.262	0.55		
C-1B-EM	1231	0.879	0.303	0.576	0.65		
C-2A	531	0.399	0.140	0.259	0.65		
C-2A-ED	61	0.121	0.093	0.028	0.23		
C-2A-EM	480	0.378	0.144	0.234	0.62		
C-2B	742	0.533	0.164	0.369	0.69		
C-2B-ED	69	0.121	0.088	0.033	0.27		
C-2B-EM	453	0.352	0.129	0.223	0.63		

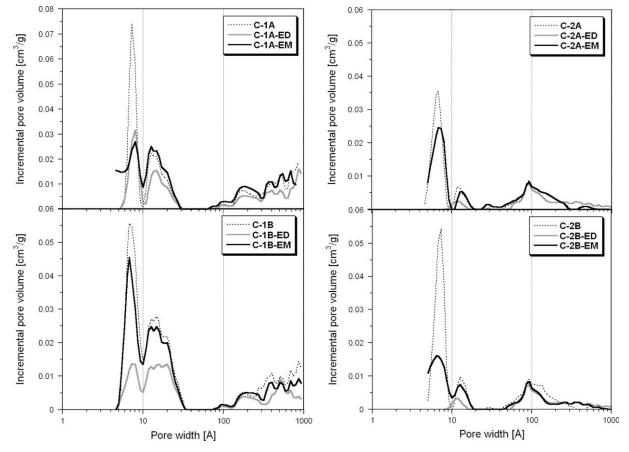


Fig. 4 - Pore size distribution for the samples before and after arsine adsorption.

sition of arsenic pentoxide, is found to sublimate. For C-1A-ED, the weight loss pattern is more complex with new well visible peaks at 350 and 400 °C. They are assigned to the decomposition of arsenic trioxide present at various pore sizes. The peak at about 200 °C can be the result of arsenic acids formation since this sample, as a result of more oxygen groups is expected to retain more water than C-1B [19]. On the corresponding sample run in moist conditions (C-1A-EM), the new feature is the presence of a peak at about 350 °C which must be linked to the decomposition of arsenic trioxide. For

C-2B-EM and, interestingly for C-2A run at the dry conditions, the peak at 200 °C is also found. That temperature also represents the decomposition of arsenic acid,  $H_4As_2O_7$  (206 °C [18]) and its formation in moist conditions is a plausible explanation, if some arsine is oxidized to  $As_2O_5$ . For C-2A-EM, no new peak is detected. For C-2B and C-2A run in the dry conditions, the weight loss patterns are much more complex than those for the C-1 series, especially that one for the latter sample. While for the C-2B-ED two peaks with maxima at about 400 and 600 °C are assigned to the decomposition of arsenic

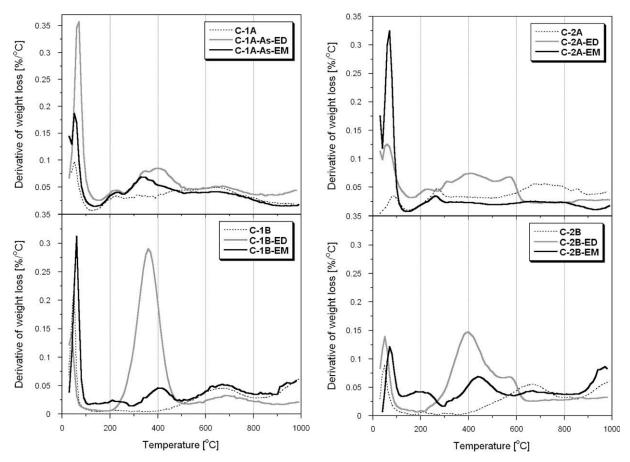


Fig. 5 - DTG curves in nitrogen for the samples before and after arsine adsorption.

pentoxide (about 315 °C [18]) and then sublimation of arsenic (617 °C [18]), respectively, the broad peak representing the continuous weight loss for C-2A in this temperature range suggests formation of other species than arsenic oxides. For this sample also, the peak at about 200 °C related to arsenic acids is present. Taking into account the high content of sulfur in this sample in the form of sulfonic and thiophene-like functionalities [9], it is plausible to assume that, in addition to arsenic oxides, arsenic sulfides are formed on the surface of this carbon. Considering all of this, the peak at ~300 °C can be attributed to arsenic trioxide and/or arsenic disulfide,  $As_2S_2$  (melting point at 307 °C [18]). The peak at  $\sim$ 600 °C can then be linked to the release of As<sub>2</sub>S<sub>2</sub> (boiling point at 565 °C [18]) and/or As<sub>2</sub>S<sub>5</sub> (sublimation at about 500 °C [18]) and sublimation of arsenic. Thus, besides arsenic oxides (tri-, as shown from DTG curves and XRD, and pentoxide from DTG curves and FT-IR spectra), sulfides are likely formed in surface reactions on the C-2A sample. Formation of sulfides is supported by a decrease in the weight loss over 600 °C where the decomposition of sulfur-containing groups, likely thiophenic [9], or basic oxygen groups is expected to occur. Although a decrease in weight loss can also be seen for the sample run in the moist conditions at which almost no arsine was adsorbed, that decrease is an apparent result of a significant amount of water adsorbed on this sample (the curves are not normalized). This decrease in weight loss suggests that those sulfur and oxygen groups take part in the reactive adsorption of arsine. This effect is not so well pronounced for the C-2B material, although some decrease in the weight loss at temperatures higher than  $600\,^{\circ}\text{C}$  is noticed.

As mentioned above, a very well-defined low temperature peak at about 200 °C for C-2A and C-1A run in dry conditions suggests the formation of arsenic acids. Its appearance on the surface can be explained by the presence of water on these carbons. The surface of C-2A is especially polar with a significant quantity of very hydrophilic surface functional groups [9]. They, together with relatively small pores and large number of oxygen groups, attract water even at ambient conditions [19]. This might be the effect of water observed at low relative humidity for cuprous oxide impregnated carbons observed by Hickey and Wiig [6]. That water enhances the amount adsorbed in so called "dry conditions" even though the porosity of the C-2 carbon is less than that of C-1. Support for this is found in the analysis of water adsorption isotherms measured on our carbons (Fig. 6). A very specific shape of the isotherm for C-2A reveals that at 30% humidity almost all accessible pores are filled whereas for other carbons a more gradual increase in the amount adsorbed is noticed. Also on C-1A much more water is adsorbed at low relative pressures than on C-1B. Stronger oxidations shift the condensation to lower relative pressure as expected [20]. This peculiar behavior of water can explain the negligible capacity of our carbons in the presence of moisture in the gas phase. Apparently water adsorbs in a significant quantity, blocks pores and thus "poisons" the active sites as suggested by Hickey and Wiig [6]. Those active sites must be the groups containing oxygen and

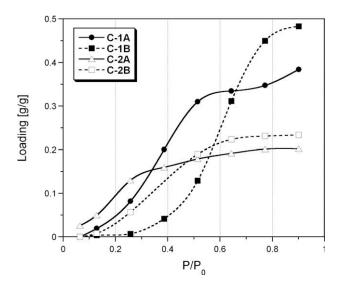


Fig. 6 - Water adsorption isotherms of the samples studied.

sulfur. The latter ones are involved in the formation of sulfides, as hypothesized above. It is interesting that only on C-2A, adsorption of AsH<sub>3</sub> was measurable in the presence of humidity, even though the adsorbed water is not favorable for AsH<sub>3</sub> retention. This suggests that the active sites of this carbon are still able to attract arsine. These sites can be only R-S sites since their affinity for water should be smaller than that of oxygen containing groups and sulfonic groups.

The oxidizing ability of our carbons can be linked to the presence of oxygen superoxide anions, which are formed from oxygen in the presence of oxygen [10,11] and possibly sulfur-containing groups. Although the latter were not analyzed in the literature to the same extent as oxygen and nitrogen containing groups [10,11], the chemical similarity in the nature of those elements, and the behavior of sulfur-containing groups in carbons [9] and graphite oxides [21] let us hypothesize that sulfur species may play a similar catalytic role as nitrogen and oxygen species.

Based on the above-discussed results, we propose that on the surface of our materials the following reactions occur.

In the absence of water, arsenic oxides are formed in reactions with active oxygen:

$$2AsH_3 + 3(C^+, O_2^-) \rightarrow As_2O_3 + 3H_2O + 3C$$
 (1)

$$2AsH_3 + 4(C^+, O_2^-) \rightarrow As_2O_5 + 3H_2O + 4C$$
 (2)

On the surface on which an activation of oxygen is even more enhanced by the presence of sulfur groups as on C-2A, we can consider:

$$As_2O_3 + (C^+, O_2^-) \to As_2O_5 + C$$
 (3)

Moreover, owing to exothermic reaction and presence of oxygen from air, the carbon surface is also oxidized as demonstrated by an increase in oxygen content and acidity.

Also, the sulfonic groups are reduced and lead to the formation of arsenic sulfides:

$$AsH_3 + R - SO_3H \rightarrow As_xS_y + H_2O$$
 (4)

In moist air, we observe additionally:

$$As_2O_5 + 2H_2O \rightarrow H_4As_2O_7$$
 (5)

$$As_2O_3 + 3H_2O + (C^+, O_2^-) \rightarrow 2H_3AsO_4 + C$$
 (6)

For reaction (6) the acidic environment and  $As_2O_5$  can be considered as catalysts [22]. As mentioned above, both those conditions exist in our systems.

#### 4. Conclusions

Based on the results presented in this paper, it was found that oxygen and sulfur-containing groups participate in arsine oxidation to arsenic tri- and pentoxide and/or in the formation of arsenic sulfides. This occurred either via activation of oxygen or a direct involvement of these groups in the reactions with arsine. The hydrophilic surface of sulfur-containing carbons, even though the challenge gas is dry gas, enhances the removal of arsine via retention of small quantity of water from the environment. On the other hand, in moist conditions, when the humidity level is increased, water totally occupies the pore system blocking the catalytic action of the surface toward oxidation, which leads to very limited or nil capacity. From a more practical point of view, these oxidized carbons demonstrate higher adsorption capacities than some commercial activated carbons [4]. Considering their relatively easy preparation, they can thus be considered as promising materials for the removal of arsine. Nevertheless, precautions should be taken here as the experimental conditions of the breakthrough tests differ from one study to another and are sometimes different from the ones encountered in industrial processes.

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